ALKALI CATALYZED CARBON GASIFICATION II.
KINETICS AND MECHANISM

Charles A. Mims

Exxon Research and Engineering Company
P. O. Box 45
Linden, NJ 07036

Joanne K. Pabst

Exxon Research and Engineering Company
P. O. Box 4255
Baytown, TX 77520

INTRODUCTION

The kinetics and mechanism of carbon gasification have been the subject of many investigations. Kinetic measurements and mechanistic interpretations are often complicated by uncertainties concerning the identity, activity, and number of gasification sites. In the previous paper, a dispersed site picture was presented for catalysis of carbon gasification by potassium. This appears to be a well-defined, reproducible system consisting of a predictable number of essentially equivalent catalytic sites, and is therefore well suited for kinetic studies. We have examined the kinetics of both gasification and oxygen exchange (believed to be an elementary step in gasification) at the catalytic sites. This paper will discuss those results and some mechanistic implications.
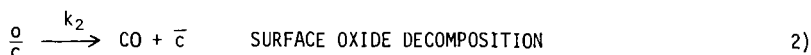
EXPERIMENTAL

The kinetic experiments were performed in a small, atmospheric pressure fixed bed reactor charged with about 0.25 g. of catalyzed char or carbon. H_2O from a syringe pump and other gases metered through a gas manifold system were mixed and preheated in the top portion of the reactor. Unreacted H_2O was removed from the product gas which was then fed directly into a GC and/or MS for analysis. Both coals and model carbons were impregnated to incipient wetness with K_2CO_3, dried in a vacuum oven, and devolatilized under N_2 at 700°C for 30 minutes.

RESULTS AND DISCUSSION

OVERALL KINETICS

It is well known that gasification of carbon by H_2O is highly product inhibited. (1) Figure 1 shows that the gasification rate increases linearly with the $(H_2O)/(H_2)$ ratio over a broad range. The impact of product inhibition must be carefully considered when treating the kinetics of these systems in integral reactors. For simplicity, the kinetic data reported in this paper were obtained in a pseudo-differential mode by feeding a mixture of H_2O and H_2 across the carbon bed at low H_2O conversions and at sufficient $(H_2O)/(H_2)$ ratio so that the reactivity of the gas did not change significantly across the bed.

In developing a mechanism for gasification, the strong product inhibition must be explained. The concept of gas/carbon oxygen exchange involving surface carbon oxides as gasification intermediates is the key to many mechanistic schemes. A simple surface oxide mechanism has been discussed frequently in the literature: (2)

$$H_2O + \bar{c} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \frac{o}{c} + H_2 \qquad \text{OXYGEN EXCHANGE} \tag{1}$$

$$\frac{o}{c} \xrightarrow{k_2} CO + \bar{c} \qquad \text{SURFACE OXIDE DECOMPOSITION} \tag{2}$$

In the context of the dispersed site picture for potassium catalyzed gasification, $\bar{c}$ is a carbon atom associated with an active catalytic site, and $\frac{o}{c}$ is the oxidized form of the active site. Upon decomposition of the surface oxide a new site is regenerated perhaps as the alkali specie becomes associated with another carbon. The number of active sites, Ct, remains approximately constant up to high carbon conversions as reflected by the flat gasification burnoff curves discussed in the previous paper.

According to this and similar mechanisms, the gasification rate is proportional to the number of surface oxides present under gasification conditions, $dc/dt \propto (\frac{o}{c})$. This scheme suggests that H_2 inhibits gasification by decreasing the number of surface oxides through the reverse oxygen exchange reaction. (Several other mechanisms have been proposed in which H_2 is thought to block active gasification sites through chemisorption.(3)) If the oxygen exchange reaction is in equilibrium and the number of surface oxides is determined by the equilibrium constant of reaction 1 (i.e. $(\frac{o}{c})/(c) = K_1(H_2O)/(H_2)$) then the relative rates of gasification of carbon by different reactants can be predicted by their relative oxygen activities. For example, the relative rates of carbon gasification in H_2O and D_2O at the same $(H_2O)/(H_2)$ and $(D_2O)/(D_2)$ ratio would be given by the ratio of the oxygen exchange equilibrium constants, i.e.

$$\frac{RATE, H_2O}{RATE, D_2O} = \frac{K_1, H_2O}{K_1, D_2O}$$

This ratio is equivalent to the equilibrium constant for the reaction $H_2O + D_2 \rightleftharpoons D_2O + H_2$, which can be calculated from thermochemical data and is plotted in Figure 2 as a function of temperature. The data for the measured rate ratios fall very near the predicted line in the temperature range studied. Oxygen activity therefore does appear to be an important factor in determining the gasification rate. This supports the idea that H_2 inhibition occurs through reversal of oxygen exchange rather than by site blocking due to chemisorption.

From the simple surface oxide mechanism represented by Equations 1 and 2, assuming a site balance Ct = $\bar{c}$ + $\frac{o}{c}$, a Langmuir-Hinshelwood type rate expression can be derived (2):

$$\frac{d(CO)}{dt} = \frac{k_1 \, k_2 \, Ct \, (H_2O)}{k_1(H_2O) + k_{-1} \, (H_2) + k_2} \quad . \tag{3}$$

For agreement with the overall gasification kinetics, this expression must be reduced to a form which reflects the linear dependence of the rate on the $(H_2O)/(H_2)$ ratio. This dictates that the $k_{-1}(H_2)$ term dominate the denominator, in which case the rate equation reduces to

$$\frac{d(CO)}{dt} = k_2 k_1 Ct \, \frac{(H_2O)}{(H_2)} \quad . \tag{4}$$

264

The $k_{-1}(H_2)$ term will outweigh the other terms in the denominator if the oxygen exchange reaction is in equilibrium, the equilibrium constant is small, and the subsequent surface oxide decomposition is slow. In addition to providing for the dependence of the rate on the $(H_2O)/(H_2)$ ratio, Equation 4 also reflects the linear dependence of the rate on catalyst loading discussed in the previous paper, and on the oxygen activity of the gas (i.e.K_1).

This simple mechanism based on the concept of oxygen exchange is useful in understanding how a number of factors can influence the gasification rate. For further evaluation of this mechanism, the assumptions which had to be made in order to reduce the rate expression to a reasonable form must be tested. This was done by studying the kinetics of the oxygen exchange reaction.

OXYGEN EXCHANGE

The oxygen exchange reactions can be readily followed using isotopic exchange techniques. For the case of $H_2O/\bar{c}$ oxygen exchange, a mixture of H_2O and D_2 is fed across the carbon bed. Since, as it will be demonstrated, oxygen exchange is very fast compared to gasification, the experiments can be performed at conditions where the gasification rate is negligible. Isotopic scrambling occurs as H_2O and D_2 undergo oxygen exchange with the catalyzed carbon according to Equation 1. In the experiments the water products (H_2O, HDO, and D_2O) were trapped out of the product stream and the gas products (H_2, HD, and D_2) were fed directly into a mass spectrometer for analysis. At gasification conditions, statistical scrambling of the isotopes between the gas and water products was observed, indicating that the reaction was in equilibrium. Under conditions at which the reaction was not at equilibrium, the rate of oxygen exchange was calculated from the rate of appearance of H in the gas products. (4)

Turnover rates (per C atom) for $H_2O/\bar{c}$ oxygen exchange were measured for Illinois char as a function of K_2CO_3 loading (expressed as K/C atomic ratio) and are shown in Figure 3. The gasification rate is plotted as well for comparison. The oxygen exchange rate increases linearly with catalyst loading until saturation which occurs at a K/C atomic ratio of approximately 0.12/1. The figure includes data for several other carbon forms as well. Below catalyst saturation the oxygen exchange rate shows very little dependence on the form of the carbon substrate. In both instances this parallels the behavior of the gasification rate (as discussed in previous paper), very strong evidence that oxygen exchange is occurring at the gasification sites. Although they were measured at a lower temperature, the rates of oxygen exchange were considerably higher than the gasification rates, indicating that the measured oxygen exchange is not rate controlling in gasification.

The kinetics of oxygen exchange occurring at the gasification sites are important in developing and evaluating an overall gasification mechanism. Figure 4 shows that oxygen exchange is first order in (D_2) and essentially independent of (H_2O). In terms of the simple oxygen exchange model, oxygen exchange occurs via Equation 1, and a Langmuir-Hinshelwood type expression can be derived for the rate of oxygen exchange:

$$H_2O + \bar{c} \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; H_2 + \overset{o}{\bar{c}}$$

$$\text{RATE} \quad = \quad \frac{k_1 k_{-1} \; C_t \; (H_2O) \; (H_2)}{k_1(H_2O) + k_{-1}(H_2)} \quad . \tag{5}$$

For the model to be consistent, the conditions imposed on the various rate co-efficients in deriving the overall rate expression (Equations 3 and 4) must apply here as well. This requires that the $k_{-1}(H_2)$ term again dominate the denominator, in which case Equation 5 reduces to

$$\text{RATE} = k_1(H_2O)Ct .\qquad\qquad 6)$$

This predicts that the oxygen exchange rate should be first order in (H_2O), in direct conflict with the data shown in Figure 4. The assumptions which were made in deriving a reasonable rate expression from the simple model were there-fore incorrect, indicating that the simple model cannot adequately describe the system. More complex oxygen exchange models can be visualized which could re-concile the data, and these will be the subject of future studies.

Kinetic studies of gasification and oxygen exchange in the CO_2-carbon system have also been performed as part of this investigation. An oxygen exchange mechanism for CO_2 gasification analogous to that discussed here for H_2O gasifica-tion has been proposed in the literature (2). Our results do support a strong analogy between the two systems. The kinetic results and mechanistic implications drawn for the CO_2-carbon system were essentially identical to those discussed here for the H_2O-carbon system.

CONCLUSIONS

Oxygen exchange is catalyzed by the potassium gasification catalyst and occurs at the same sites as gasification. Product inhibition of gasification occurs through reversal of the oxygen exchange reaction by the product rather than by chemisorption. This implies the participation of a critical surface oxide in gasification. However, this critical oxide does not react with the gas phase via Equation 1 as the dominant mode of oxygen exchange.

REFERENCES

1. F. J. Long and K. W. Sykes, J. Chim. Phys. 47, 361 (1950)

2. P. L. Walker, Jr., F. Rusinko, Jr., L. G. Austin, Advan. Catalysis 11, 133 (1959)

3. For discussion, see H. H. Lowry, ed., "Chemistry of Coal Utilization, Supplementary Volume," John Wiley and Sons, Inc., New York-London, 1963, p. 929

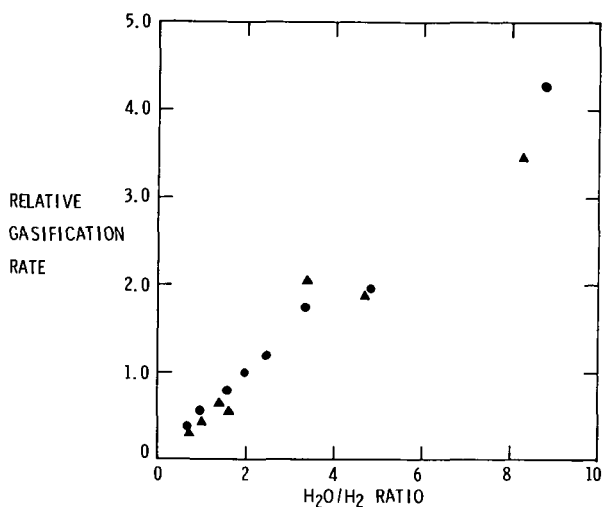4. A. A. Orning and E. Sterling, J. Phys. Chem. 58, 1044 (1954)

FIGURE 1. PRODUCT INHIBITION OF GASIFICATION RATE.
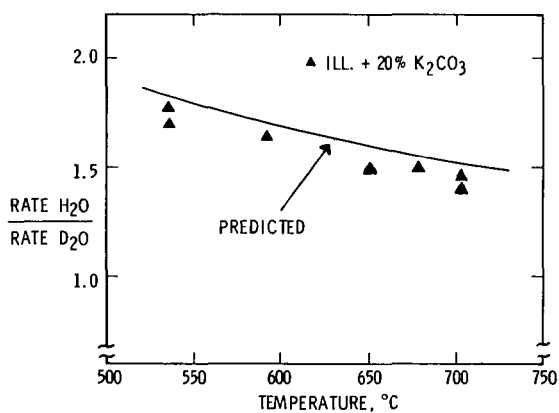▲ ILLINOIS + K_2CO_3, ● SPHEROCARB + K_2CO_3
700°C.

FIGURE 2. DEPENDENCE OF GASIFICATION RATE ON OXYGEN
ACTIVITY: RELATIVE GASIFICATION RATES IN H_2O AND
D_2O. SOLID LINE – PREDICTED VALUES. ▲ MEASURED
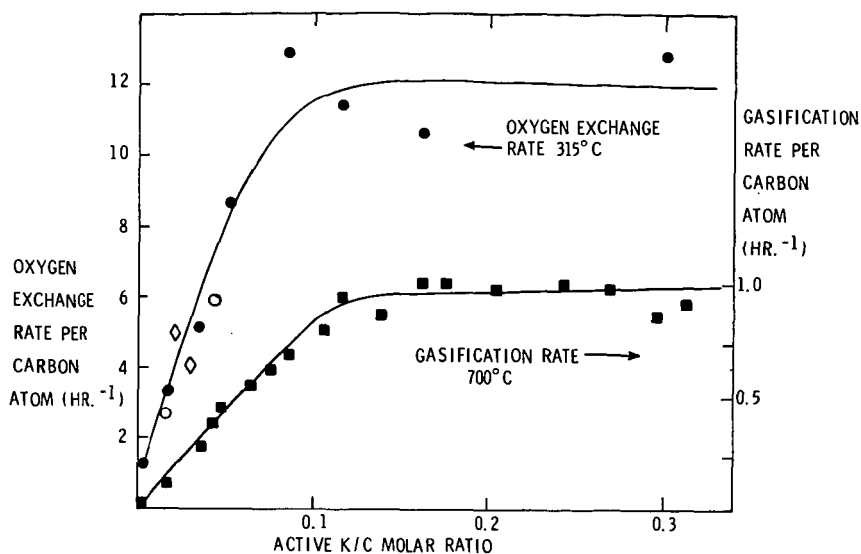VALUES.

FIGURE 3. DEPENDENCE OF H_2O-D_2 OXYGEN EXCHANGE RATE ON CATALYST LOADING AND COMPARISON WITH GASIFICATION RATE. ●, ■ ILLINOIS COAL + K_2CO_3, ○ ACTIVATED CHARCOAL + K_2CO_3, ◊ SPHEROCARB + K_2CO_3
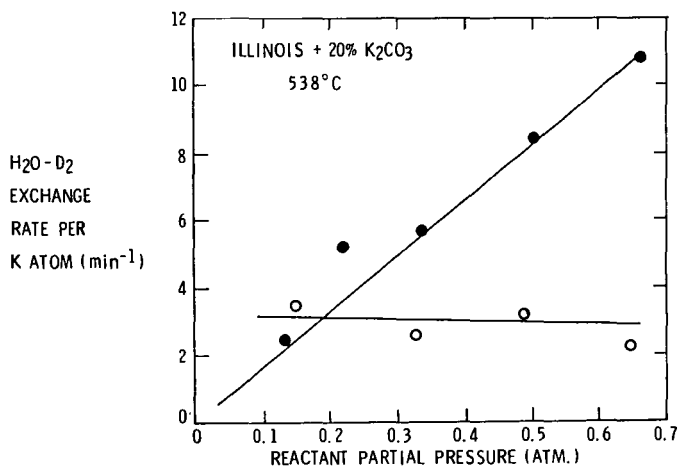

FIGURE 4. DEPENDENCE OF H_2O-D_2 OXYGEN EXCHANGE RATE ON REACTANT PARTIAL PRESSURE. ● D_2, ○ H_2O.